

-OFFICE OF NAVAL RESEARCH
END-OF-THE-YEAR REPORT
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT
for
N00014-95-1-0306

The Reactivity and Dynamics of Gaseous Clusters
Subtitle: The Dynamics and Controlled Shaped Synthesis of Gaseous and Colloidal
Nanoparticles

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OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 4131015
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Contract/Grant Title: The Reactivity and Dynamics of Gaseous Clusters
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- a. Number of papers submitted to refereed journals, but not publishes: 4
- b. + Number of papers published in refereed journals (for each, provide a complete citation): 2
- c. Number of books or chapters submitted, but not yet published: 0
- d. +Number of books or chapters published (for each, provide a complete citation): 1
- e. +Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 0
- f. Number of patents filed: 0
- g. +Number of patents granted (for each, provide a complete citation): 0
- h. +Number of invited presentations (for each provide a complete citation):
- i. +Number of submitted presentations (for each, provide a complete citation): 0
- j. +Honors/Awards/Prizes for contract/grant employees (list attached):
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
- k. Total Number of Full-Time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:
Graduate Students: 3
Post-Doctoral Associates: 0
Including the number of,
Female Graduate Students: 1
Female Post-Doctoral Associates: 0
the number of
Minority* Graduate Students: 1
Minority* Post-Doctoral Associates: 0
and, the number of
Asian Graduate Students: 0
Asian Post-Doctoral Associates: 0
- l. +Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant).

+Use the letter and an appropriate title as a heading for your list, e.g.:

b. Published Papers in Refereed Journals, or, d. Books and Chapters published

Also submit the citation lists as ASCII files, preferably on a 3" or 5" PC-compatible floppy disk

+Minorities include Blacks, Aleuts, Amindians, Hispanics, etc. NB? Asians are not considered an under-represented or minority group in science and engineering.

Part 1

a. Papers Accepted or Submitted to Refereed Journals (and not yet Published)

1. Temer S. Ahmadi, Zhong L. Wang, Travis C. Green, Arnim Henglein and Mostafa A. El-Sayed, "Shape Controlled Synthesis of Colloidal Platinum Nanoparticles". Science
2. Temer S. Ahmadi, Stephan L. Logunov, and Mostafa A. El-Sayed, "Picosecond Dynamics of Colloidal Gold Nanoparticles", J.Phys. Chem
3. Temer S. Ahmadi, Zhong L. Wang, Arnim Henglein, and Mostafa A. El-Sayed, "Synthesis of 'Cubic' Colloidal Platinum Nanoparticles at Room Temperature", Chemistry of Materials.

b. Papers Published in Refereed Journals

1. Valey F. Kamalov, Reginald Little, Stephan L. Logunov and Mostafa A. El-Sayed, "Picosecond Electronic Relaxation in CdS/HgS/CdS Quantum Dot Quantum Well Semiconductor Nanoparticles", J.Phys.Chem., **100**, 6381-6384 (1996)
2. John E. Freitas, Hyun Jin Hwang, and Mostafa A. El-Sayed, "The Wavelength Dependence of the Rate of Internal Energy Redistribution during the Photodissociation of 3-Iodopyridine", J.Phys.Chem, **99**, 7395-7406, 1995.
3. Clifton K. Fagerquist, Dilip K. Sensharma, Mostafa A. El-Sayed, Angel Rubio, and Marvin L. Cohen, "Enhancement of Metallic Silver Monomer Evaporation by the Adhesion of Polar Molecules to Silver Nanocluster Ions", J Phys Chem., **99**, (19) 7723-7730, 1995.

c. Books or Chapters Submitted by not yet Published

None

d. Books or Chapters Published

none

e. Technical Reports Published

none

f. Patents Files

none

g. Patents Granted

none

h. Invited Presentations

1. March 6, 1994: National Research Council Committee on the Free Electron Lasers, Washington, D.C., "Advanced Photon Sources in Physical Chemistry (invited talk)
2. June 25, 1994: American Society of Photobiology, Scottsdale, AZ, "Molecular Mechanisms of the Protein Catalysis and Specificity of the Subpicosecond Retinal Photoisomerization in the Primary Step of Bacteriorhodopsin Photosynthesis" (invited talk)
3. July 21, 1994: IVth IUPAC Symposium on Photochemistry, Prague, Czech Republic, "Molecular Mechanisms of the Protein Catalysis and specificity of the Subpicosecond Retinal Photoisomerization in the Primary Step of Bacteriorhodopsin Photosynthesis" (invited speaker)
4. August 21, 1995: American Chemical Society, Chicago, IL, "Molecular Mechanism of the Proton Pump of the Other Natural Photosynthetic System." (invited talk)
5. December 15, 1994: Tel Aviv University 30th Year Anniversary Symposium, Tel Aviv, Israel, "Molecular Mechanisms of Solar-to-Electric Energy Conversion of the Other Photo Synthetic System in Nature" (invited speaker)
6. March 20-24, 1995: Mini-Symposium, Institute for Molecular Science, Okazaki, Japan, "On the Molecular Mechanism of Solar-to-Electric Energy Conversion by the Other Photosynthetic System in Nature, Bacteriorhodopsin".(invited speaker)
7. May 11-14, 1995: Seventh International Conference On Time Resolved Vibrational Spectroscopy, Santa Fe, New Mexico, "Perspective on the frontiers in Time Resolved Vibration Spectroscopy". (invited speaker)
8. July 31, 1995. The 17th International Conference on Photochemistry, "Energy Redistribution in the Transition State of Half Collision Reactions Involving Iodine". London, England (invited speaker)
9. August 21, 1995: American Chemical Society, Chicago, IL, "Molecular Mechanism of the Proton Pump of the Other Natural Photosynthetic System." (invited talk)
10. October 23-27, 1995. The International Conference on Molecular Spectroscopy, "The Mechanism of the Protein Catalysis of the Retinal Photoisomerization in Bacteriorhodopsin". Yokohama (invited speaker)
11. December 14-16, 1995 New Developments in Ultrafast TR Vibrational Spectroscopy. "The Molecular Mechanism of the Proton Pump in Bacteriorhodopsin Photosynthesis". Tokyo, Japan (invited speaker)

12. December 17-22, 1995 International Chemical Congress of Pacific Basin Societies, Kauai, Hawaii "Studies on the Molecular Mechanisms Involved in the Protein Catalysis of the Subpicosecond Retinal Photoisomerization and the Proton Pump in Bacteriorhodopsin". (Invited speaker)

i. Submitted Presentation

none

j. Honors/Awards/Prizes

1. Charles A. Coulson Lecture, University of Georgia, Athens, GA (1994)
2. Recipient of the Harris Award, University of Nebraska, Lincoln, NE (1995)
3. The Harris Lecture, University of Nebraska (1995)
4. Advances in Chemical Physics Lecture, Rutgers, NJ (1995) The 1995 Boston College University lecture (1995)
5. Invited to be and accepted as Member of Editorial Advisory Board for Chemical Physics Letters, (1995)
6. Invited to be and accepted as Member of International Advisory Board, Russian Chemical Bulletin, Moscow, Russia (1995)
7. Invited to be and accepted as Member of Advisory Board, Bulletin of the Chemical Society of Japan, Tokyo, Japan (1995)
8. Invited to be and accepted as a Member of Advisory Board, Journal of Saudi Chemical Society, Riyadh, Saudi Arabia (1995)
9. Chairman of Review Committee, Lawrence Laboratories, Berkeley, CA (1995)
10. Chairman of Review Committee, Chemistry Department, University of Oregon, Eugene, Oregon (1995)
11. Officer, Division of Physical Chemistry, IUPAC General Assembly Meeting, Guildford, UK (1995)
12. Chairman, Awards Committee, National Academy of Science Award in Chemical Sciences (1995)

k. Number of Full-time equivalent Graduate Students and Post-Doctoral Associates supported during this period under this grant number:

Total	<u> 2 </u>	Postdoctoral	<u> 0 </u>
Female Graduate Students	<u> 1 </u>	Female Postdoctoral	<u> 0 </u>
Minority Graduate Students	<u> 1 </u>	Minority Postdoctoral	<u> 0 </u>
Asian Graduate Students	<u> 0 </u>	Asian Postdoctoral	<u> 0 </u>

1. Other Funding

1. DOE - "Time Resolved Laser Studies on the Proton Pump Mechanism of Bacteriorhodopsin" \$135,000 4/1/95-3/31/96
2. NSF - "Real Time Clocking of Energy Redistribution in Molecules Falling Apart" \$90,000 3/1/95-2/29/96

Part II

- a. Principal Investigator: Professor M. A. El-Sayed
- b. Current telephone number: (404)894-0292
- c. Cognizant ONR Scientific Officer: Dr. Peter Schmidt
- d. Brief description of project:

In order to design new strategic materials with specific properties, we need to understand the binding forces that exist in mixed atoms or molecules not present in conventional material. Thus our aim is to understand the adhesive and cohesive forces holding atoms or molecules together in unconventional nanoparticles that do not usually bind together in conventional macroscopic materials. In the broad sense, we like to understand the forces involved in adhesion and cohesion on an atomic level by studying the structure, stability, and the rapid electronic motion in nanoparticles. Due to the large surface to volume ratio, these particles tend to have different properties not present in the bulk nor of the individual atoms or molecules making these nanoparticles. Thus they offer us an opportunity to unravel new properties with new potential applications.

The aim of our present research is to synthesize and study the forces between atoms or molecules within nanoclusters. These forces determine the dynamic properties and thus the potential uses of the nanoparticles. In the past several years, we have confined our studies to gaseous clusters and studied the dynamics of their dissociation and their chemical reactivities. During the past year, we have expanded our activity to include the synthesis and study of the dynamics of excitation relaxation in colloidal nano-particles, both semiconductor and metallic. The synthetic method we use involves a competition between nucleation of the atoms in the metallic nanoparticles or the semiconductor molecules in the semiconductor nanoparticle and the capping process of the surface with polymeric molecules. The faster the capping process, the smaller would be the average size of the clusters formed. The forces that control the shapes of nanoclusters by capping agents are to be examined.

The expansion in our research activity last year has resulted from our move to Georgia Tech where we found an excellent TEM facility that enabled us to determine the structures of the nanoparticles synthesized in solution.

e. Significant Results During Last Year:

1. Picosecond Electronic Relaxation in CdS/HgS/CdS Quantum Dot Quantum Well Semiconductor Nanoparticles (VG1, VG2, VG3)

Subpicosecond photo-excitation of CdS/HgS/CdS quantum dot quantum well nanoparticles at wavelengths shorter than their interband absorption (390nm) photobleach spectrum at longer wavelengths (440-740 nm). The photobleach spectrum changes and its maximum red shifts with delay time.

The above results are explained by the rapid quenching of the initially formed laser excited excitons by two types of energy acceptors (traps); one is proposed to be due to CdS molecules at the CdS/HgS interface, and the other trap is the HgS molecules present in the CdS/HgS/CdS well.

2. Shape-Controlled Synthesis of Colloidal Platinum Nanoparticles (VG4, VG5, VG6, VG7)

The importance of controlling the shape of the metallic nanoparticles in the field of catalysis is obvious. In this work, we found that not only the size but also the *shape* of the platinum nanoparticles can be controlled by changing the ratio of the concentration of the capping material to that of the metal ions in the reductive synthesis of colloidal particles in solution at room temperature. Different shapes are observed: tetrahedral, cubic, irregular-prism, icosahedral and/or cubo-octohedral. The distribution of these shapes varies as the concentration ratio of the capping material to that of the platinum cation is changed.

3. Picosecond Dynamics of Photoexcited Electrons in Colloidal Gold Nanoparticles (VG8)

Colloidal gold nanoparticles with an average radius of 15 nm have a surface plasmon absorption band at 530 nm. Excitation by laser pulses of 450 fs duration, and wavelength of 600 or 380 nm 'bleached' the plasmon band and produced a transient absorption at the wings of the 'bleach' spectrum (see VG8). From the observed optical transient absorption results we conclude that the coherence of the surface plasmon electron waves is destroyed rapidly due to electron-electron scattering leading to hot incoherent electrons. The 'hot' electrons relax via electron-phonon coupling in 2.5 ps, and the phonon-phonon relaxation of the lattice occurs in >50 ps.

f. Proposed Work for Next Year:

We are presently studying two types of colloidal nanoclusters, metallic and semiconductors. Different sizes, shapes, and compositions are being synthesized and the structures of which are to be determined. In addition, using our ultrafast laser facility that we have put together at Georgia Tech, we are to measure the dynamics of the rapid electronic and excitonic transport processes present in the different types of nanoclusters as a function of size, shape, and composition. Three different types of spectroscopic and structural techniques are planned for the different studies:

- a. Transient absorption or fluorescence from which the dynamics of the excitons, electrons, and holes will be examined.
- b. Time resolved optical, Raman, and FTIR studies from which the structure of the traps or of the capping material will be examined.
- c. In collaboration with Professor Z. L. Wang of Georgia Tech microelectronic laboratory, we plan to do structural studies of these nanoparticles synthesized under different conditions and with different capping material

G. Graduate Students

Reginald Little (African American) and Janet Petroski

Unique Results and Methodology of Work Carried Out during the Past Support Period:

A. Picosecond Electronic Relaxation in the CdS/HgS/CdS Quantum Dot Quantum Well Semiconductor Nanoparticles

Multi-layered quantum dots were prepared and characterized recently by Mews and co-authors [1]. They are composed of two semiconductor materials, the material with the smaller bulk band gap (e.g. HgS) is embedded between a core and an outer shell of the material with the larger band gap (e.g. CdS). This nanostructure is a new material of low-dimensional semiconductor particles. These particles combine features of quantum dots and quantum wells named quantum dot quantum well (QDQW) [1]. Scientifically, the understanding of the spectroscopy and the excitation transport in quantum dots [2], [3] and quantum wells [4], [5] is important due to quantum size effects and their low-dimensionality. In addition, they are also important to their potential applications in microelectronics. Electronic relaxation in CdS quantum dots was studied extensively [6], [7], [8], [9], [10]. Fast exciton dynamics in semiconductor quantum wells was the subject of recent reports [4], [5], [11].

It was shown [12] that the linear absorption of the QDQW composite particles, having diameter of between 5 and 12 nm, differs considerably from the sum of the linear absorptions of the respective subunits. Schooss et al [13] developed an extended theoretical approach for calculating the 1s-1s electronic transition in spherical semiconductor quantum dots. They proposed a model of effective-mass approximation with the Coulomb interaction of electron and hole and finite potential wells at the particle boundaries. They were able to describe the absorption spectra of QDQW in a reasonable manner. Energies and wavefunctions of the 1s-1s transition were determined [13]. The wave functions for both electrons and holes are found to change with a size of the particle. The maxima of amplitudes of wave functions of both electrons and holes were found in the region of the intermediate layer (HgS), so that a quantum well is formed between the core and the outer shell of the semiconductor with larger band gap (CdS).

Eychmuller et al [14] had shown the transient photobleaching of CdS/HgS/CdS particles using nanosecond flash photolysis apparatus. They observed the transient

bleaching between 600 and 700 nm with UV excitation. In this work, we determined the picosecond dynamics of the CdS/HgS/CdS semiconductor particles. Initial transient photobleaching was found to depend on the excitation wavelength. The decay rate of the transient photobleaching was found to be wavelength dependent with the faster decay at short wavelength. The observed fast dynamics is explained in terms of exciton relaxation in the quantum well formed by the thin intermediate layer. (See VG1, 2 and 3)

VG₁ shows the absorption spectrum of CdS, CdS.HgS, and CdS.HgS.Cd nanoparticles during the course of their synthesis. VG₂ gives the temporal behavior of the spectral diffusion of the negative absorption (bleaching) of the different excited species in the mixed CdS/HgS/CdS system. It shows that the initial excitons formed by excitation at 390 nm is rapidly trapped in a time faster than our time resolution (400 fs). The first trap (A) (arrow 1 and 2 in VG₂) with large distribution (due to the large distribution of the nanoparticle size and structure) lives for a few picoseconds (VG₃). The second trap B (arrow 3 in VG₂) lives for a longer time and is the trap that leads to the fluorescent emission and is previously assigned to the HgS well. We assign Trap A to CdS molecules at the CdS/HgS interface.

B. Shape control of Metallic Nanoparticles

Colloidal metal particles are of interest because of their use as catalysts [16], photocatalysts [17], adsorbents and sensors [18], ferrofluids [19], and the applications in optical [20], electronic [20], and magnetic devices [18]. Among metals, platinum is by far the most versatile catalyst used in both laboratory and industry [21]. Platinum colloidal nanoparticles have been known for decades [22]. Most of the studies on platinum particles have been focused on the optical properties, dynamics and kinetics of growth, and control of size which is directly linked to their catalytic behavior [23].

Many methods for the synthesis of colloidal platinum nanoparticles, with different degrees of size control, have been developed over the past two decades. Furlong et al. [24] have compared various methods of Pt colloids synthesis and studied the effect of temperature on the particle size. It was shown that the average particle size increases with increasing temperature. The particles studied were in the range of 3-13 nm in diameter.

Although the morphology of colloidal gold has been studied in the past [25; 26], no shape-controlled synthesis of gold particles has yet been reported. However, a recent study showed the formation of triangular and hexagonal shapes of two dimensional platinum islands formed on Pt(111) [27,28]. This study indicates that the formation of triangular and hexagonal islands is related to the temperature of the surface upon which they grow. In particular, it was shown that the formation of these islands were kinetically controlled at surface temperatures below 700K, and thermodynamically controlled at higher temperature [29] thus, indicating that control of the rate of deposition and the thermodynamic properties of the deposited material could lead to control over the shape of the islands. Wang et. Al [29] showed that Pt nanoparticles on SiO₂ and Al₂O₃ supports exhibit cubic-like shapes. These particles have rounded corners with {110} facets, and {100} curved surfaces.

- In our work, we have made colloidal platinum nanoparticles with controlled shapes. By changing the ratio of the concentration of the capping material (sodium polyacrylate) to that of Pt²⁺ (as K₂PtCl₂), we were able to change the shape of the platinum nanoparticles in preparation in aqueous solution at room temperature.. Particles with tetrahedral, cubic, irregular-prism, icosahedral and/or cubo-octahedral shapes have been observed in samples prepared under different conditions.

We have prepared platinum colloidal nanoparticles which have cubic or tetrahedral shapes in abundance of 80% and 70% relative population, respectively. These samples are prepared by changing the ratios of the concentration of the capping polymer. The TEM images are shown in VG4 and VG5. VG4 shows the cubic particles which are the dominant shapes in sample in which the concentration ratio, r , of the polymer to that of Pt²⁺ is 1. A 'close-up' TEM picture of a cubic particle with fairly sharp corners and {100} facets is shown in the inset of VG4. VG5 shows the abundance of tetrahedral shapes in sample 2 in which r is 2.5. The inset in VG5 shows the diffraction pattern of the image which shows the particle has {111} facets of a tetrahedral particle.

We have measured the shape and size distributions of the particles from the TEM images. VG6 shows the relative population abundance of the different shapes of the particles in the three samples prepared with $r = 1, 2.5, 5$ (samples 1, 2, 3 respectively). Sample 1 formed up to 80% cubic particles. In sample 2, we see an abundance of the

tetrahedrons with some small percentages of polyhedrons (icosahedrons and/or cubo-octahedrons) and irregular-prism. Sample 3, in which $r = 5$, contains a mixture of irregular-prisms, tetrahedrons, and polyhedrons. Polyhedral structures are predicted to be the most stable structures for metallic colloids [30]. However, in our samples we do not observe unusual abundance of these structures. (The reason for this might be that the shape is kinetically rather than thermodynamically controlled. We are trying to investigate the mechanism of formation of the different shape at the moment.) VG7 gives the size distribution for each shape.

Relaxation of Plasmon Electrons in Gold Nanoparticles (VG8)

- The transient optical bleach and absorption is studied as a function of time after exciting plasmon electron in gold particle of 15 nm in size.
- Rapid scattering of the coherence of the excited plasmon electrons (<400 fs)
- The incoherent hot electrons formed relax in 2.5 ps by electron phonon scattering.
- The phonon-phonon relaxation occurs in a time > 750 ps.

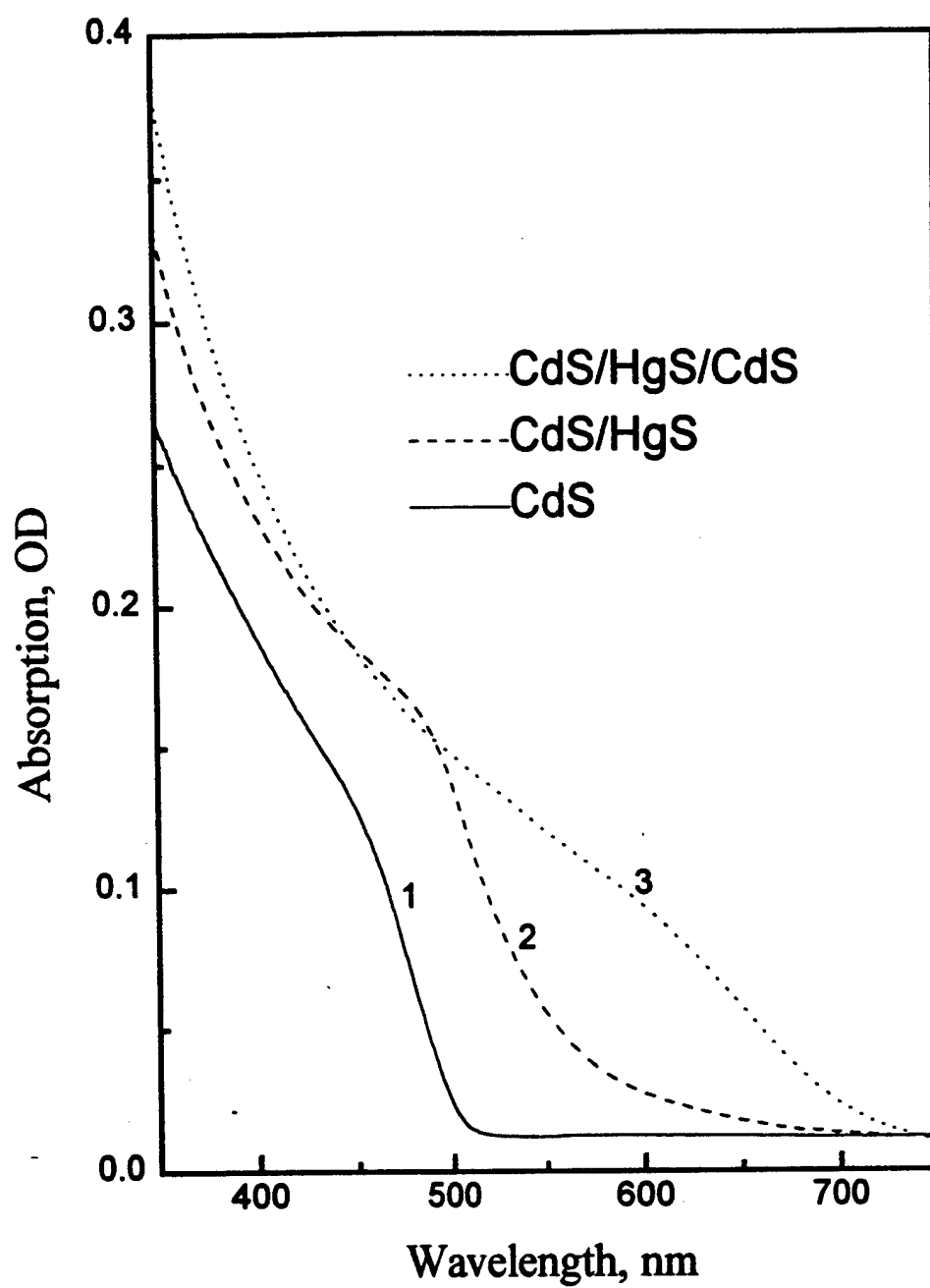
• References

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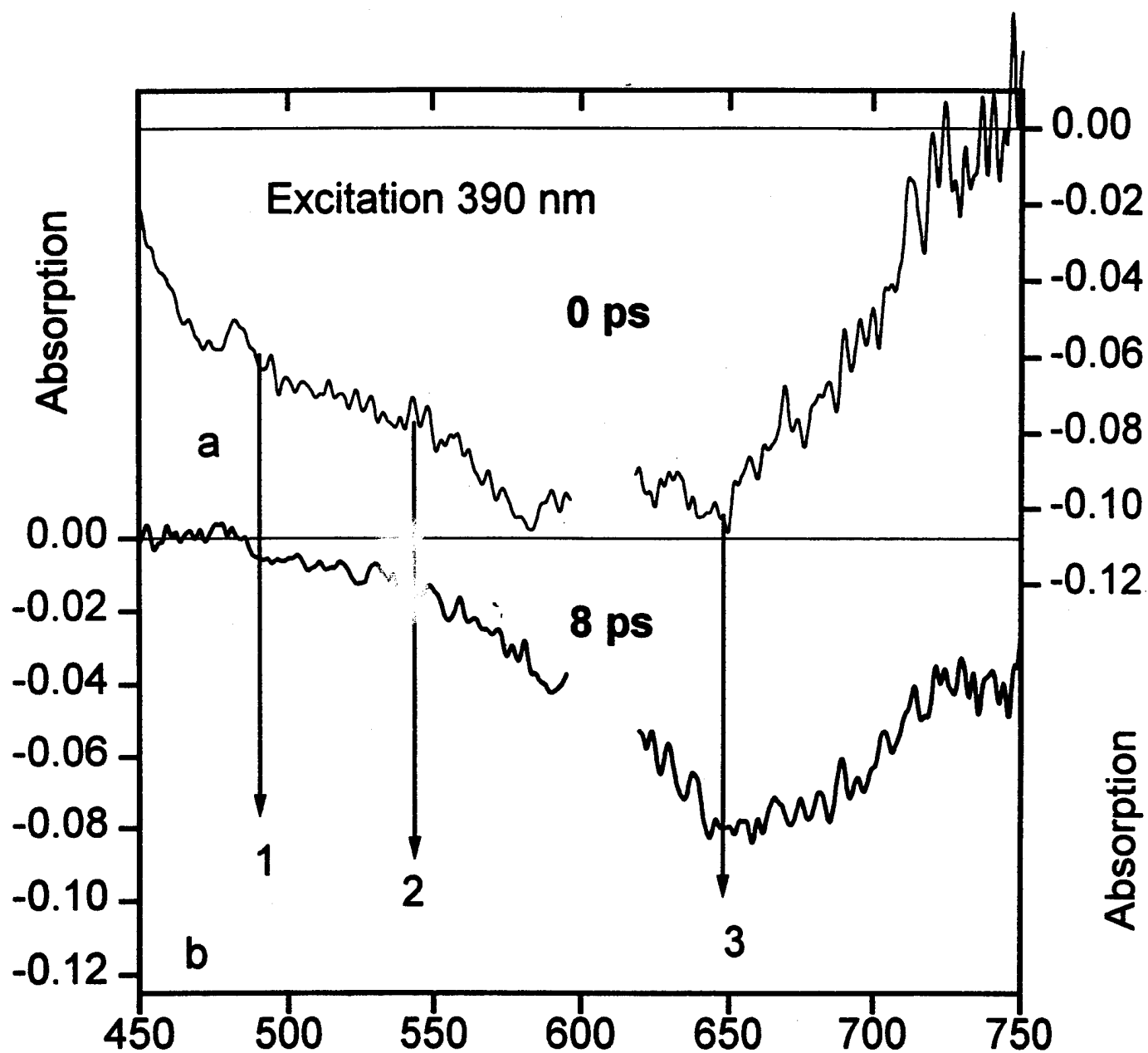
VG1: Absorption Spectra of Quantum Dot - Quantum Well Nanoparticles

Absorption spectra of CdS (1), CdS/HgS (2) and CdS/HgS/CdS (3) colloids in aqueous solution. T = 300K. From their spectrum, the average size of the CdS particles are determined to be ~6 nm.



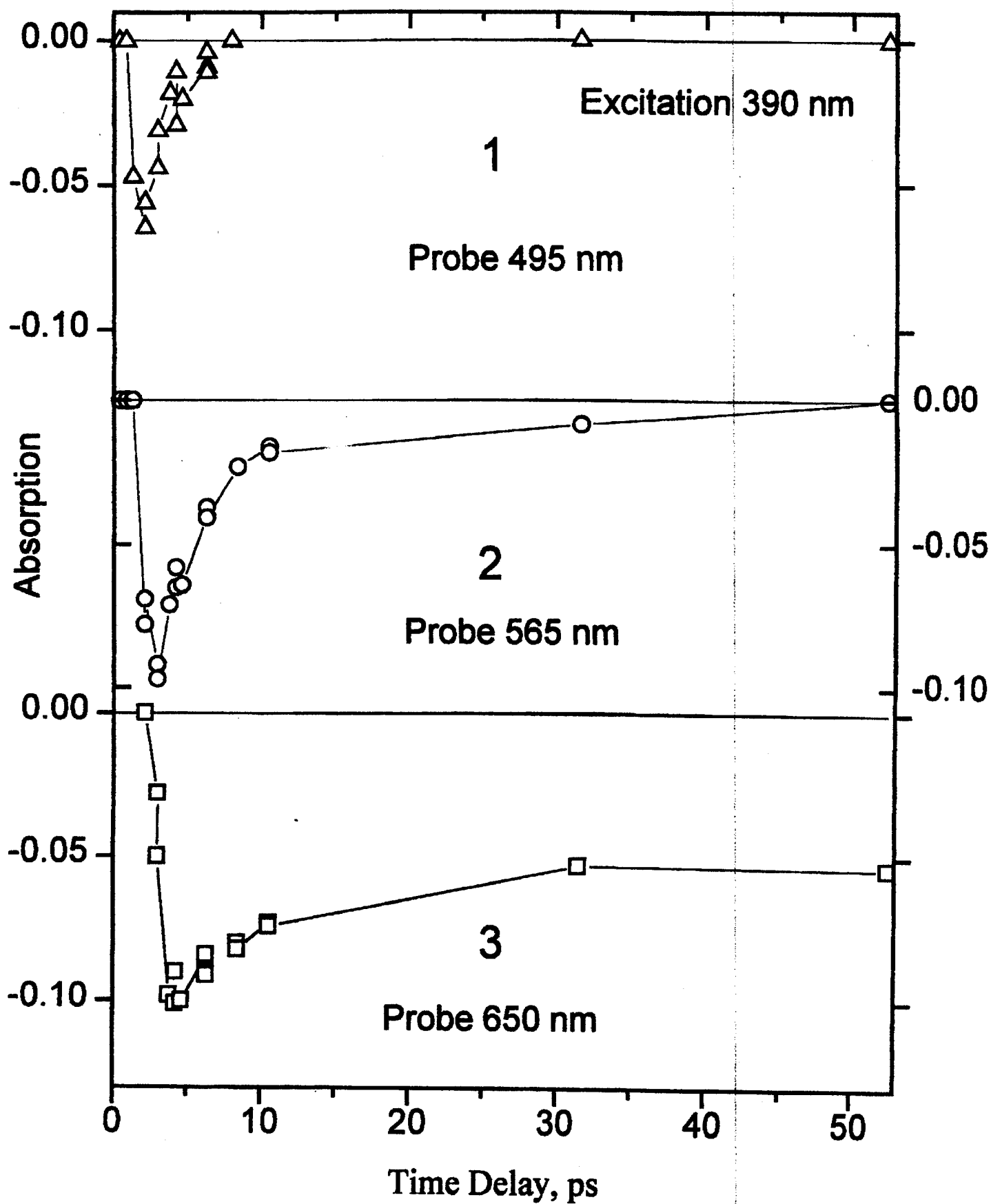
VG2: Excitation Dynamics in the CdS/HgS/CdS Quantum Dot-Quantum Well Nanoparticles

Transient bleaching band of CdS/HgS/CdS in glycerol/water glass at 9K at zero delay (a) and at 8.5 ps delay (b) after excitation at 390 nm (photon energy 3.18 eV). The fact that no bleaching is observed at 390 nm but is observed at longer wavelengths suggests rapid trapping of the original exciton in a time shorter than our 0.3 ps pulse width by large distribution of lower energy traps. This gives rise to the observed bleaching in (a). At longer delay, spectral diffusion due to further energy transfer from the high energy to the low energy traps takes place. The temporal behavior of these traps absorbing at three different wavelengths labelled 1, 2, and 3 is given in VG3.



VG3: Temporal behavior of the Trapping-Detrapping Dynamics of the Excitation in the CdS/HgS/CdS Nanoparticles

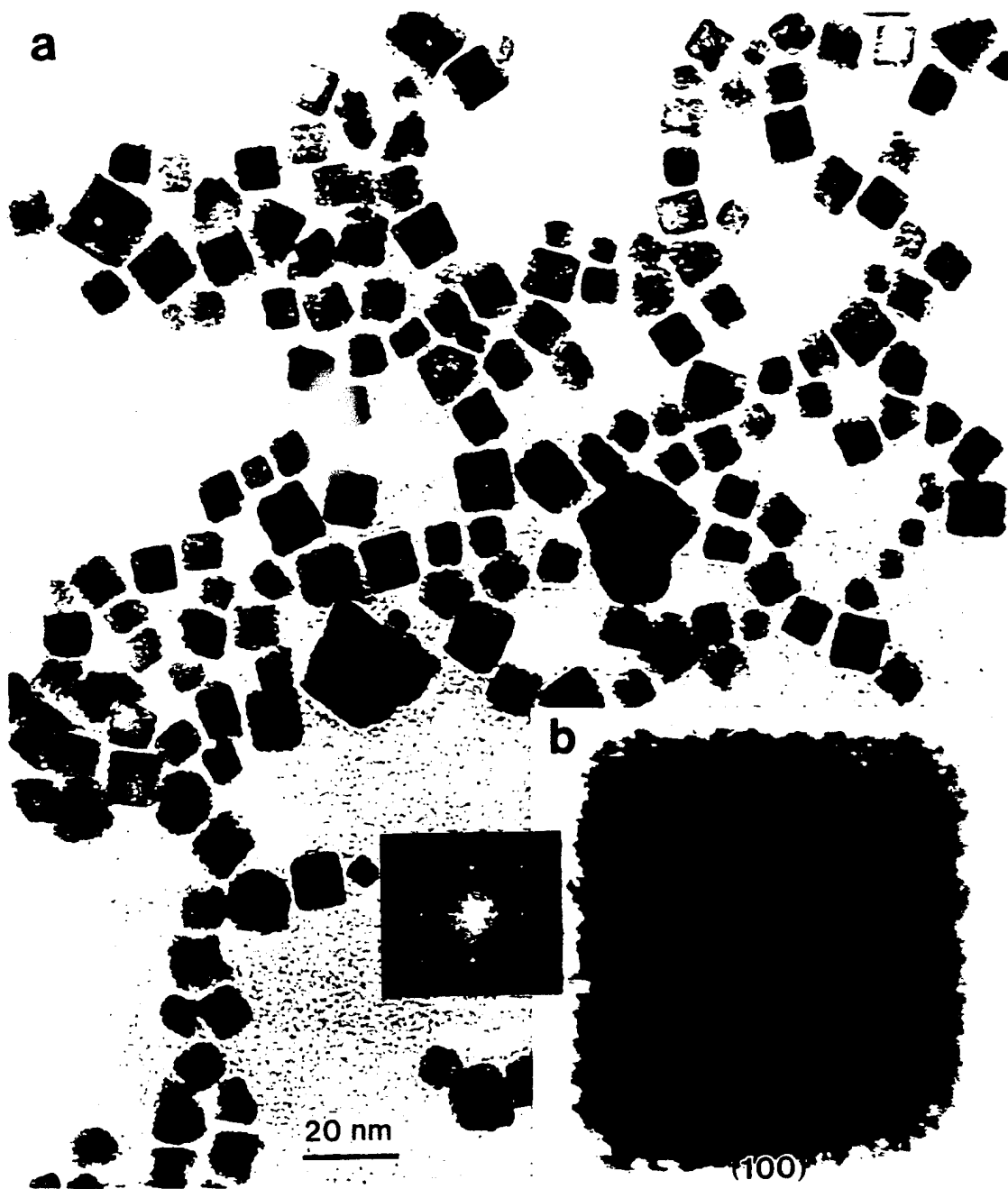
The rise and decay of the bleach of traps absorbing at different wavelengths marked by arrows 1 (495nm); 2 (565nm); and 3 (650nm) in VG2 (in glycerol/water glass at 9K.) Excitation was carried out at 390 nm. The results suggest two main traps; one with a lifetime of a few ps (marked by 1 and 2 in VG2); and one that lives longer than our time scale (marked by 3). Its position and the limit on its lifetime suggest that it is the trap that fluoresces with a lifetime of 50 ns (Weller et al)-and was suggested to be the HgS well. The picture we propose is that the initial excitation is rapidly trapped by trap 1 and 2 which further decays in a few ps to the lowest energy trap (trap 3) which is the HgS well. We propose that traps 1 and 2 are CdS molecules at the CdS/HgS interface.



VG4: Shape Control of Platinum Nanoparticles: “Cubic Nanoparticles”

(a) A TEM image of platinum nanoparticles synthesized with initial concentration ratio r of the capping polymer to Pt^{2+} of 1. It shows the abundance of cubic particles.

(b) Shows the diffractogram of one cube and the development of its {100} facets.



VG5: Shape Control of Platinum Nanoparticles “Tetrahedral Platinum Nanoparticles”

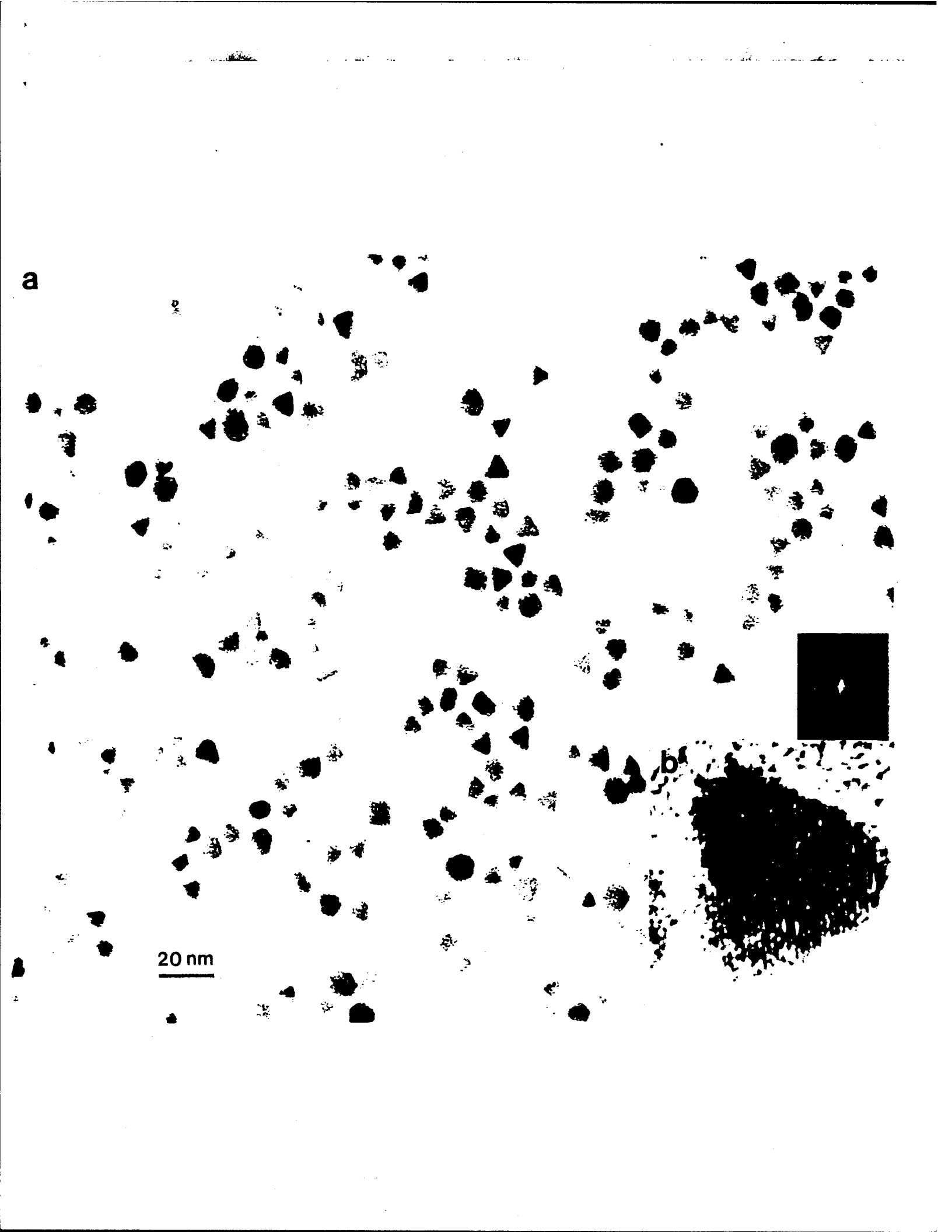
(a) A TEM image of sample 2 (in which $r = 2.5$) indicating the abundance of tetrahedral shapes.

(b) Shows the diffractogram and the {111} facets of a tetrahedron.

a

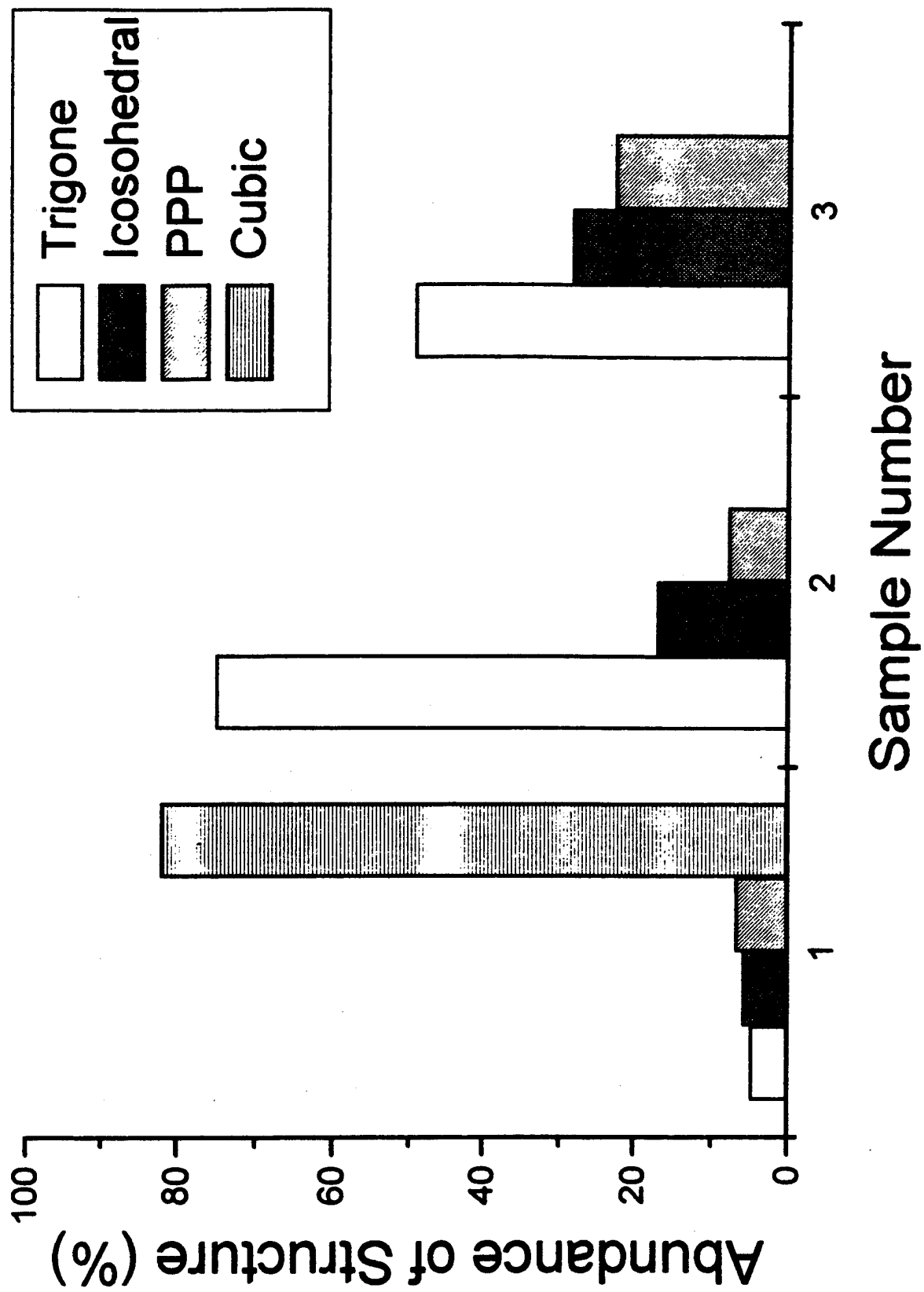
20 nm

b



VG6: Shape Distribution as a Function of Capping Material Concentration

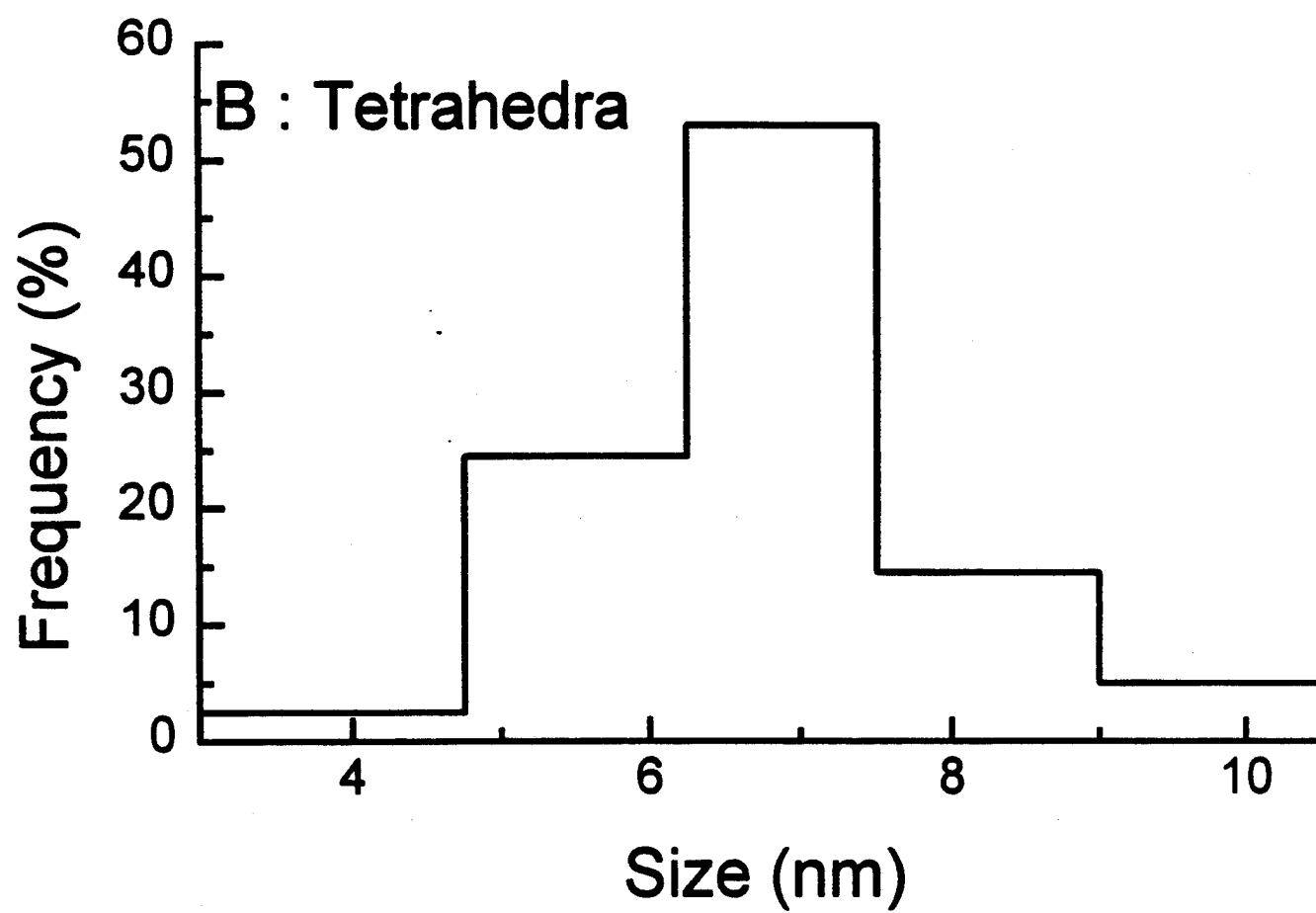
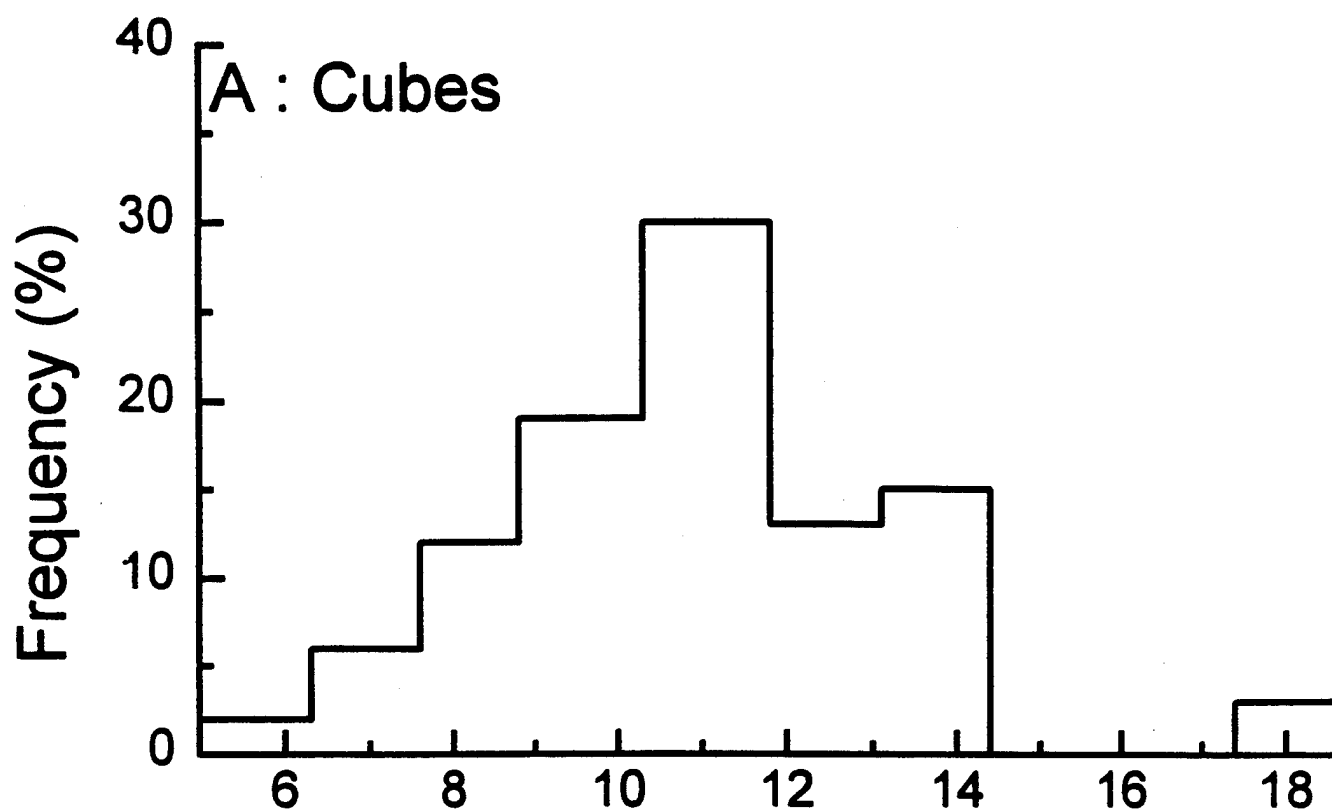
A histogram of the different shapes of sample (1) in which $r = 1$, sample (2) in which $r = 2.5$; and sample (3) in which $r = 5$. It is evident that cubes are predominant in sample 1, and tetrahedrons are predominant in sample 2. (r is the concentration ratio of capping polymer to that of the pt salt.)



VG7: The Size Distribution of the Cubic Particles and Tetrahedrons

(A) The size distribution of the cubic particles formed in sample 1.

(B) The size distribution of tetrahedrons formed in sample 2.



VG8: Relaxation of Electronic Plasmon Excitation in Gold Nanoparticles

- **Bleach (negative absorption) occurs at different wavelength (560 nm) from excitation wavelength (600 nm).**
- **This suggests a rapid loss of coherence of plasmon excitation (in <400 ps, laser pulsewidth).**
- **The decay of the relaxed hot electrons (the bleach and wing spectra) occurs in 2.5 ps (see inset) by electron-phonon coupling.**
- **A longer decay component (see inset) occurs in >50 ps and assigned to phonon-phonon relaxation.**

